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RESULTS OF THE COINJECTION OF PCI AND SYNTHETIC TITANIUM DIOXIDE PRODUCTS FOR PROTECTION OF THE HEARTH OF ROGESA Nº 5 BF AFTER STOP FOR RELINING[1]

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Abstract

At Rogesa (Dillingen, Germany) blast furnaces Nº 4 and Nº 5 a mixture of pulverized coal and small amounts of synthetic titanium dioxide (Rutilit NF) has been injected simultaneously in order to protect the hearth from premature erosion. This new technique is applied since May 2008 by using the PCI grinding and injection equipment. Sachtleben Chemie GMBH, Duisburg (Germany) has developed its "Rutilit" range of Synthetic produced material which contains mainly Titanium dioxide for large-scale industrial use. The particle geometry and low average particle size of around 20 µm of these synthetic TiO_2 sources make them particularly suitable for continuous injection via the tuyeres. This new method permits rapid repair of the damaged area if a "hot spot" occurs and prolonged significantly the life time of the BF hearth. In July 2010 Nº 5 blast furnace was stopped for relining after a campaign of 13 years and a cumulative production of 29 Mt of HM. The dissection of the hearth walls by core samples shows the characteristics of different refractory material as well as the effects of long term synthetic Titanium application. This paper is a common report from AG der Dillinger Hüttenwerke, Rogesa, Dillingen, Germany and Sachtleben Chemie GMBH, Duisburg, Germany. It examines the benefits of a long term coinjection of pulverized coal and synthetic Titanium dioxide (Rutilit NF) at Nº 5 blast furnace and the inspection of the hearth after stop for relining.

Key words: Blast furnace; Titanium dioxide; Hearth protection; Repair; Rutilit.

RESULTADOS DA CO-INJEÇÃO DE CARVÃO PULVERIZADO E DE PRODUTOS DE DIÓXIDO DE TITÂNIO SINTÉTICO, PARA PROTEÇÃO DO CADINHO DO ALTO-FORNO Nº 5 DA ROGESA, APÓS PARADA PARA NOVO REVESTIMENTO

Resumo

Nos alto-fornos nº 4 e nº 5 da Rogesa (Dillingen, Alemanha), foi injetada em simultâneo uma mistura de carvão pulverizado com pequenas quantidades de diôxido de titânio sintético (Rutilit NF), com o intuito de proteger o cadinho contra erosão prematura. Esta nova técnica é aplicada desde maio de 2008, usando a injeção de carvão pulverizado moído e o equipamento de injeção. A Sachtleben Chemie GMBH, Duisburg (Alemanha) desenvolveu sua gama de "Rutilit" de material de produção sintética, que contém principalmente dióxido de titânio para uso industrial em larga escala. A geometria das partículas e a reduzida média do tamanho das partículas (aprox. 20 µm) destas fontes sintéticas de TiO_2 tornam elas particularmente adequadas para injeção contínua através das ventaneiras. Este novo método permite a reparação rápida da zona danificada se ocorrer um ponto quente (*hot spot*), e prolongou significativamente a vida útil do cadinho dos alto-fornos. Em julho de 2010, o alto-forno nº 5 foi parado para reforma, após uma campanha de 13 anos e uma produção acumulada de 29 megatoneldas de gusa. A dissecação das paredes do cadinho por amostras de tarugos mostra as características de um material refratário diferente, bem como os efeitos da aplicação prolongada de titânio sintético. Este documento é um relatório conjunto da AG da Dillinger Hüttenwerke, Rogesa, Dillingen, Alemanha e da Sachtleben Chemie GMBH, Duisburg, Alemanha. Ele examina as vantagens de uma co-injeção prolongada de carvão pulverizado e de dióxido de titânio sintético (Rutilit NF) no alto-forno nº 5 e a inspeção do cadinho, após parada para novo revestimento.

Palavras-chave: Alto forno; Titanium dioxide; Proteção do cadinho; Reparação; Rutilit.

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1 INTRODUCTION

1.1 Rogesa - Ironmaking Facilities

The company Roheisengesellschaft SAAR (Rogesa), with a yearly production capacity of 4,6 million t of hot metal (HM), is a joint venture of the AG DER Dillinger Huettenwerke, the major European heavy plate producer, and Saarstahl AG, one of the most important manufacturers of long products in the world. It is located at the site of Dillingen in the south west of Germany.
Table 1 shows some characteristic items of both blast furnaces operated by Rogesa at the site of Dillinger Hütte.

Table 1. BF Nº 4 and Nº 5 most significant parameters

	BF Nº 4	BF Nº 5
Year of construction	1974/2003	1985/1997
Restart after relining	Oct.2003	Oct. 2010
Reason of revamping	BF relining	BF relining
Nominal production	6200 t (metric)	7200 t
Number of tap holes	2	2
Working volume	2358 m³	2934 m³
Hearth diameter	11,2 m	12 m
Number of tuyeres	30	32

Blast furnace Nº 4 was restarted after enlargement in 2003.(1) The BF Nº 5 was relined from July to October 2010 after its second campaign which had an interim repair in 2006. The reducing agents used are coke and pulverized coal, injected via a total of thirty lances at BF Nº4 and thirty two lances at BF Nº 5 at tuyere level.
Table 2 shows the results of the two parts of the second campaign which had to be interrupted by an interim repair in 2005 because of progressive wear of the hearth walls after eight years of operation.

Table 2. BF Nº 5 most significant parameters

		Second Campaign		Second Campaign-Total
Begin of campaign		Aug.29.1997	Jan.30.2006	Aug.29.1997
End of campaign		Dec.12.2005	Jul.12.2010	Jul.12.2010
Time intervalls		before interim repair	after interim repair	total
Campaign	year	8,3	4,5	12,8
Total HM production	M t	18,9	10,2	29,1
Production	t/m³ w.v.	7318	3570	10888
Hearth diameter	m	12	12	
Hearth area	m²	113,1	113,1	
Working height	m		24,7	
Working volume	m³	2581	2581	
Inner volume	m³	3067	3067	
Number of toyeres		32	32	
Number of tap holes		2	2	
Daily production	t/24h	6577	6335	6493
Hearth area productivity	t/m² 24h	58,2	58,0	58,1
Working volume productivity	t/m³ 24h	2,55	2,45	2,25
Burden Sinter	kg/tHM	1177	1079	1143
Pellets	kg/tHM	199	307	236
Lump ore	kg/tHM	207	198	204
Reductant rate	kg/tHM	475	476	475
Coke	kg/tHM	323	306	317
Small coke	kg/tHM	24	27	25
PCI	kg/tHM	128	143	133

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2 INPUT OF TITANIUM BEARING PRODUCKTS AT ROGESA BLAST FURNACE

In 2005 several hot spots, higher temperatures were measured and corresponding thin residual carbon thickness was estimated. In order to operate the blast furnace properly until the scheduled date of the interim repair, following measures were consequently taken into action:

- charging lump Ilmenite (32 % TiO_2) with burden into the furnace;
- injecting "Rutilit F 50" (50 % TiO_2) via several tuyeres.

Because of the good results using the Rutilit F50 in 2005[2,3] to reduce local hot spot formation and for preventive action, Rogesa and Sachtleben developed the coinjection of Rutilit NF together with the pulverized coal (PCI). From July 2008 to July 2010 was injected a mixture of Rutilit NF and pulverized coal into blast furnace Nº 4 and Nº 5. During this time the total injection quantity of PCI and Rutilit NF was 0,8 -1,2 kg/t HM.
The coinjection of pulverized Rutilit NF and coal with a flow-rate 155 Kg/t HM, i. e. 0,8 -1,2 kg Rutilit NF/t HM did not show any negative influence onto the reductants consumption of the hot-metal production. The HM-temperature has a constant level of 1.465°C – 1.485°C (2.669 F – 2.705 F). The slight fluctuation of the Ti content in the hot metal, which has been in the range of 0,02 – 0,08%, has been caused both by the thermal state of the blast furnace and by the Rutilit NF coinjection. The TiO_2 content in the slag during Rutilit NF coinjection was at any time maintained below 0,9%, which is a significant quality criterion for processing and sale of the granulated slag as an additive for cement products.[4]

Table 3. Time interval of injection titanium bearing products

	Time interval	BF Nº4	BF Nº5	Input	Average addition/ Injection rate
Lump Ilmenit	June 4th to Nov. 1th 2005		Repair of Hot Spot	Charging with the burden	
Rutilit F 50	July 1th to Oct. 7th 2005		Repair of Hot Spot	Separate Injection Sytem	3 Kg/t HM
Rutilit NF	July 20th 2008 to July 17th 2010	Preventive application	Preventive application	Coinjection with PCI	0,8 to 1,2 Kg/t HM

The analysis of the injected material is shown in Table 4. Rutilit F 50 and Rutilit NF are synthetic produced material, which contain mainly Titanium dioxide. The main grain size of the Rutilit products is in a range between 5 and 70 µm with an average particle size of 20 to 30 µm. The injection of fine-particulate TiO_2 (Rutilit) sources via the tuyeres directly in the vicinity of the hearth zone is a more effective method of importing TiO_2 into the BF. This technique offers a lot of advantages.[5,6] The various Rutilit products are suitable for a range of different uses, varying from preventative application (RUTILIT NF) up to and including high-speed reactions to "hot spots" (Rutilit F50).[7-10]

Table 4. Chemical analysis of Rutilit NF and Rutilit F 50

	TiO_2	Fe_2O_3	SiO_2	Al_2O_3	CaO , MgO	Moisture content
	%	%	%	%	%	%
Rutilit NF	50-60	max. 10	max. 25	max. 5	max. 8	22 - 28
Rutilit F50	45-55	max. 40	max. 20	max. 6	max. 6	< 2

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3 RESULTS OF DISSECTION OF THE HEARTH

The interim repair of the hearth walls in 2005 had to be performed in an emergency situation because of the progressive wear after 8 years of operation. The main cause therefore was the use of low quality coke.[3]
The reason why different carbon block qualities were used is the consequence of the non-availability of sufficient high quality carbon in a short delivery time.
The lower 3 layers is a high conductive semi graphite, layers 4 to 6 is a plain carbon with low conductivity, layer 7 and 8 are a graphite blocks with very high conductivity.
Additionally there was installed a 250 mm ceramic cup of nitride bonded high alumina bricks (Figure 1).

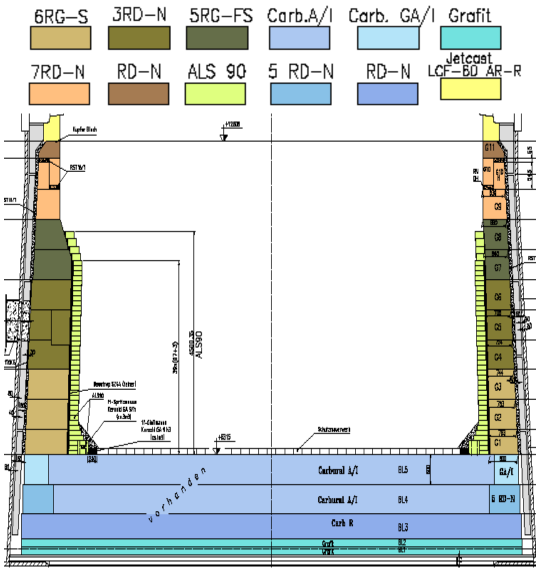

Figure 1. Hearth design of the previous campaign.

The two pictures (Figure 2) show the hearth walls at the clearing opening in August 2010 (tuyere 28 and 30).

- the formation of the brittle layer is well to be seen mainly in layers Nº 4 to 6 where the plain carbon with the low heat conductivity was installed;
- the higher conductive semi graphite in layer 1 to 3 shows lower sensitivity;
- in front of the brittle layer there exists still a part of the carbon block with a scull to the inside.

Figure 2. Hearth walls with brittle layer.

The lower row Nº 1 at the bottom corner shows definitively no wear and is still in it's original state.
There existed still remains of the ceramic cup (Figure 3).

Figure 3. Carbon block at the corner bottom/wall.

The measurements of the wear of the hearth walls at different locations of the circumference show similar results: (top to down).

- few wear at rows Nº 7 and 8 (graphite is not resistant to liquid iron, high heat conductivity: 45 W/m K prevents the formation of a brittle layer);
- pronounced wear at rows Nº 4 to 6 (low conductivity: 13 W/m K);
- very few wear at rows Nº 1 to 3 because of the protection by the ceramic cup and further high conductivity of 37 W/m K.

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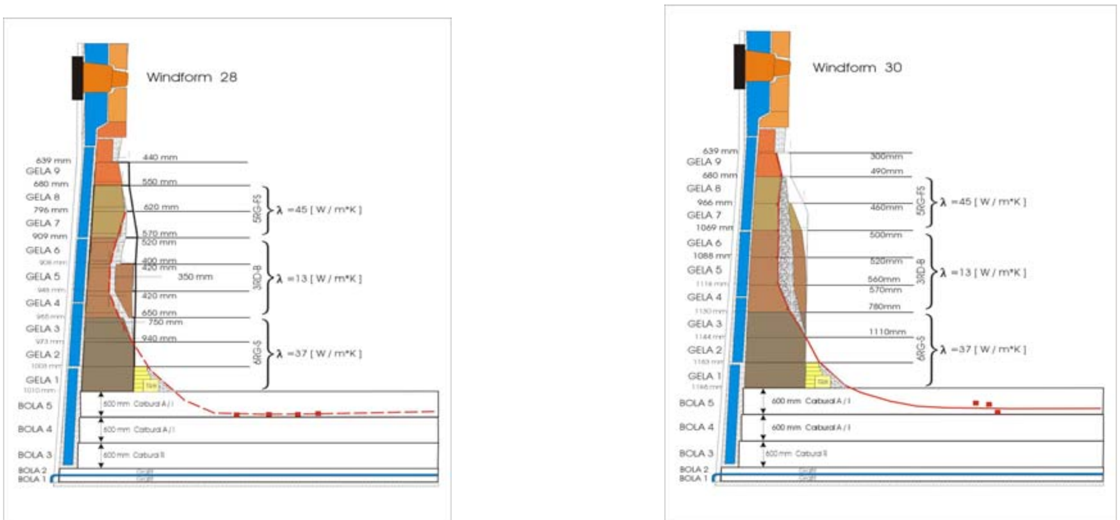

Figure 4. Measurements of the wear of the hearth walls.

The Figures 5 and 6 show the following operational data which can influence the shown hearth temperatures:

- CSR-value of the coke; low CSR-values increase the hearth temp. because of the increase of the peripheral flow of the hot metal;
- downtime percentage influences the hearth temp. when the furnace is stopped;
- Rutilit NF addition to the injected pulverized coal.

In the first half of the year 2008 there was no Rutilit NF input, the temperatures remained stable or increased only slightly.
In the second half of the year 2008 Rutilit NF input was at approximately 1 kg/t HM, temperatures remained constant or decreased a little at the end of 2008 in section 5, in section 6 occurred a definitive decrease of the temperatures; coke quality was stable all the year 2008 with CSR over 60%.
In the first half of the year 2009 because of the economic crisis the frequent stoppages of the furnace leaded to a decrease of the temperatures, but in the second half of 2009 the coke quality became worse; consequently, the temperatures rose.
In 2010 the wear of the hearth proceeded; an interruption of the Rutilit NF injection in January 2010 caused an increase of the temperatures.
Coke quality problems continued and frequent short stoppages were also not favourable for the hearth.
From mid June in 2010 Rutilit NF injection was stopped leading to a sharp increase of the temperatures.
This was a desirable effect because of the dissolution of the protective layers of TiCN in order to improve favours the casting of the salamander

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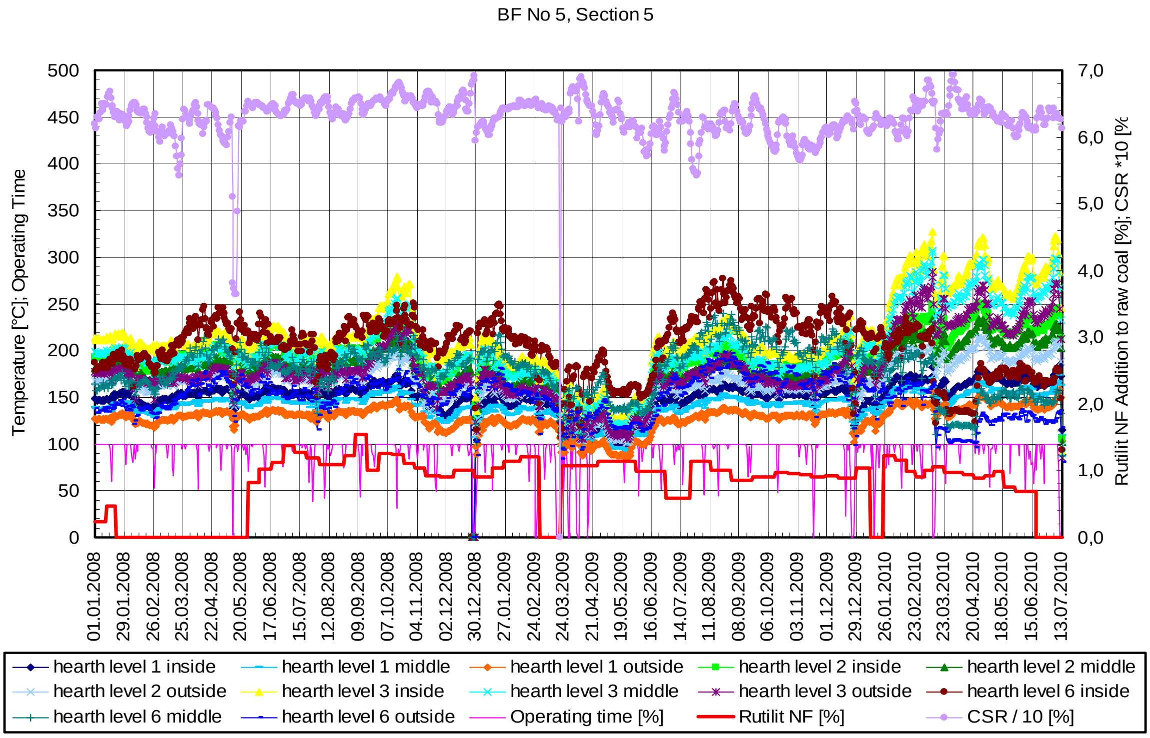


Figure 5. Temperature measurements and operation data (section 5).

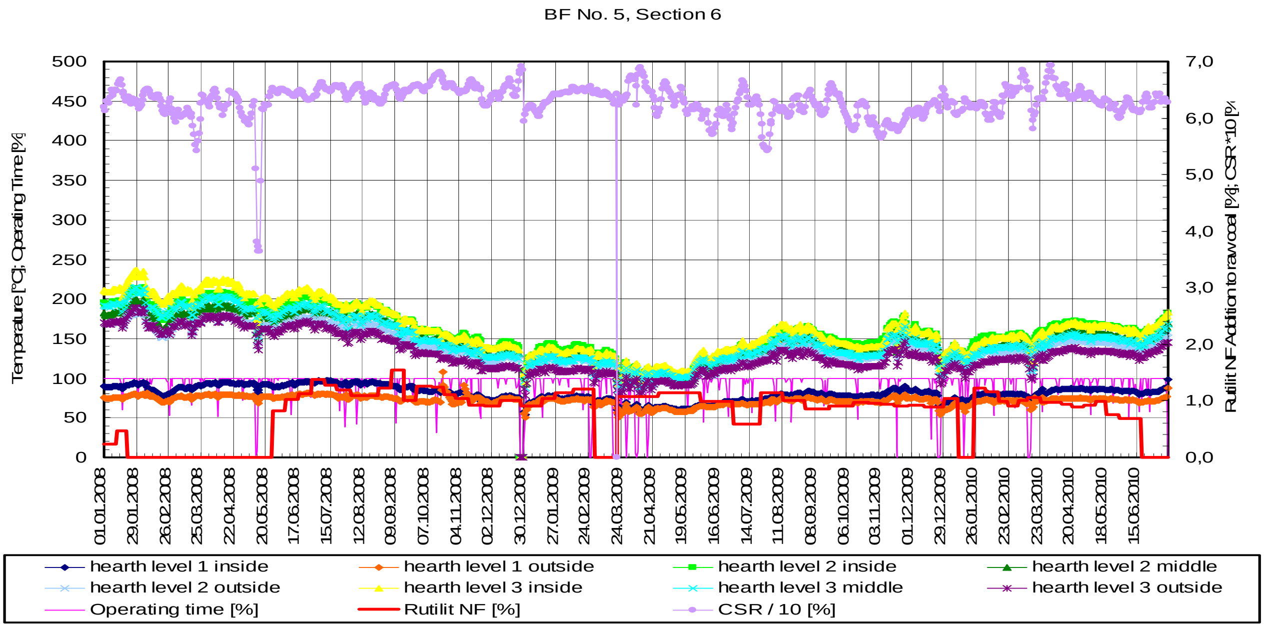


Figure 6. Temperature measurements and operation data (section 6).

Three series of core hole drilling at 5 different levels were performed in order to study the behaviour of the different carbon qualities.(11) After the campaign the samples were examined chemically and physically and also the existence of titanium compounds could be detected. The addition of Rutilit NF was stopped four weeks before the stop of the furnace in order to “clean“ the hearth, but some contents of Titanium could be verified in the core samples.

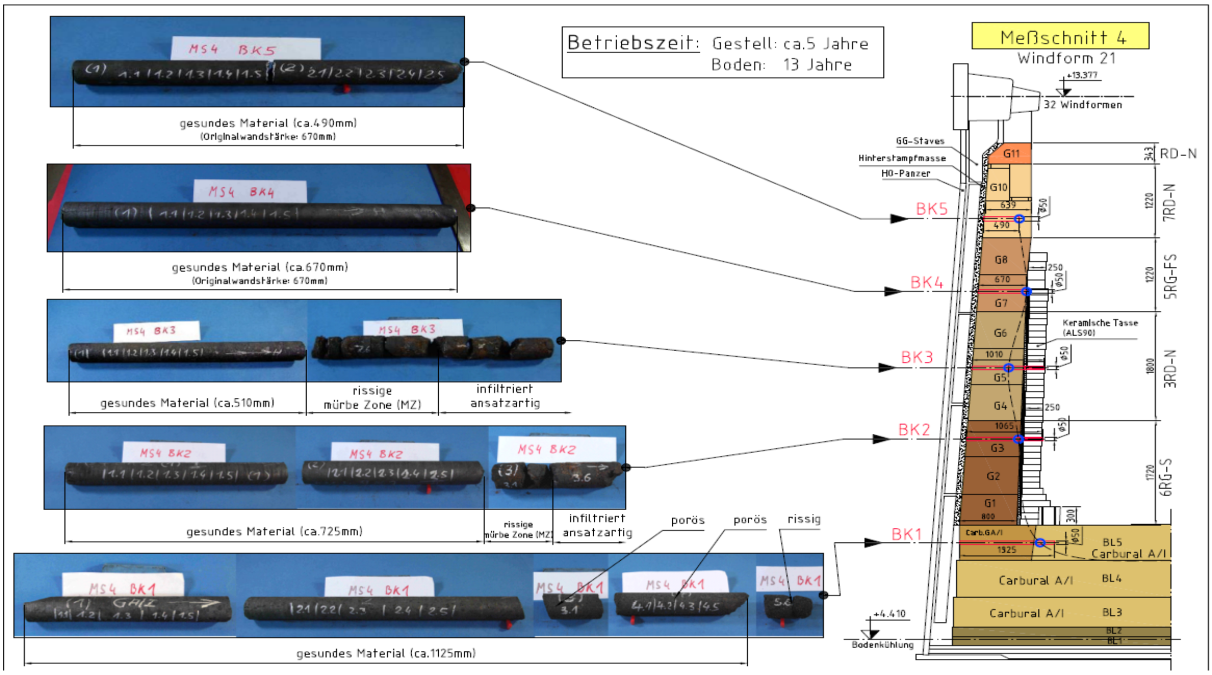


Figure 7. Core boring samples from the hearth walls.

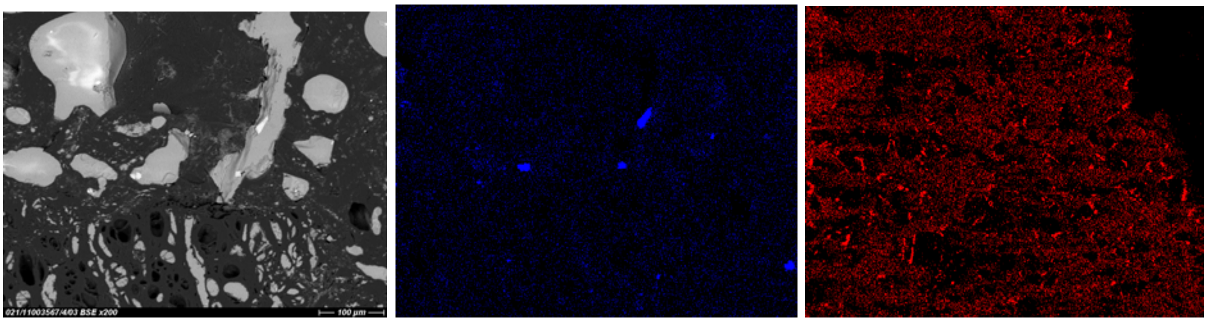
4 ELECTRON-MICROSCOPIC EXAMINATION AND CHEMICAL ANALYSIS FROM 2 CORE SAMPLE OF A BF Nº 5

The objective of the electron-microscope test is above the infiltration of Titanium compounds in the core samples and determining the distribution of the elements by means of energy-dispersive analysis (EDX)

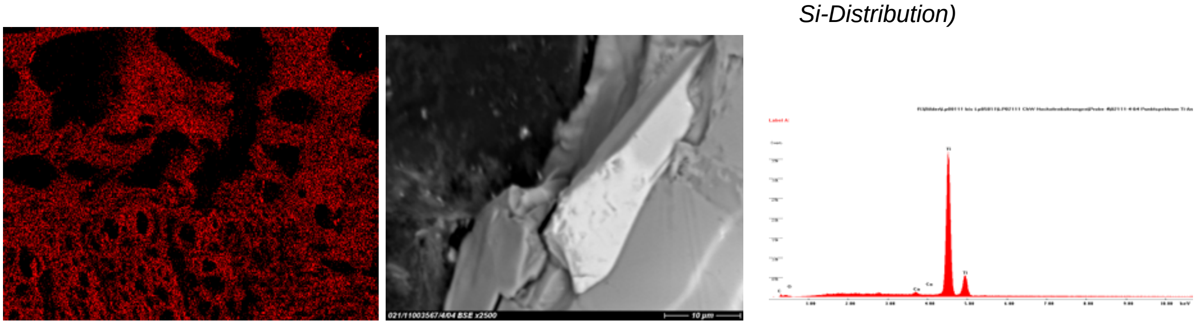
4.1 Investigation of the Sample Section 4 from Hearth Level 5 Inside

Figure 8. Core boring sample from hearth level 5 inside.

Inside the first surface phase amounts of Titanium was detected. The Images E show higher magnifications of this area with a Titanium grain and the element distribution for image F are the Mappings F to H. The EDX graph from the grain proofs only the presence of Titanium and no other elements and Oxygen. For this case is mentioned that the presence of nitrogen is difficult to detect with the used EDX, the lower detection limit is approximately 10%.



E: SEM contrast of material *F: Ti-Distribution* *G: Ca-Distribution (same like Al, O and Si-Distribution)*



H: C-Distribution *I: SEM –Detail of TiCN grain* *J: EDX-pointgraph of the Ti-enrichment from picture I*

Figure 9. Investigation of the sample MS4.

4.2 Investigation of the Sample Section 6 Bottom Layer (BK 1 in Figure 7)

Figure 10. Core boring sample section 6 from bottom layer inside.

The general view shows three main phases of the sample. This is clear shown at the SEM picture in the contrast of material (F). There is a dark carbon phase, a bright iron phase and a calcium/aluminium/silicon phase in a grey level manner.

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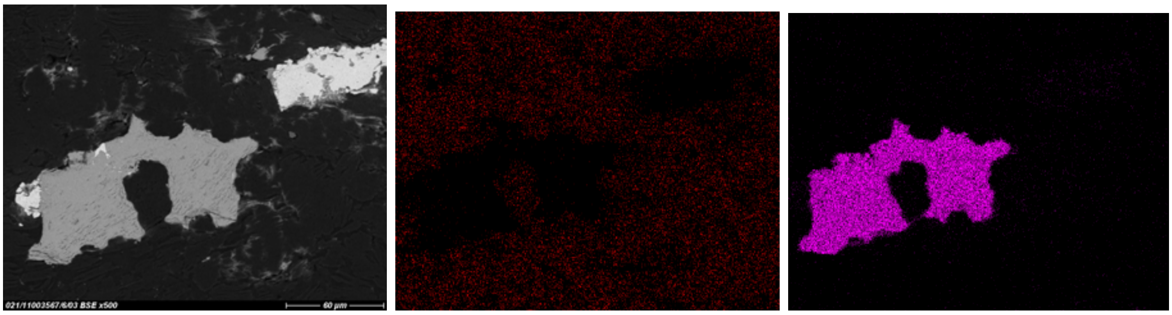
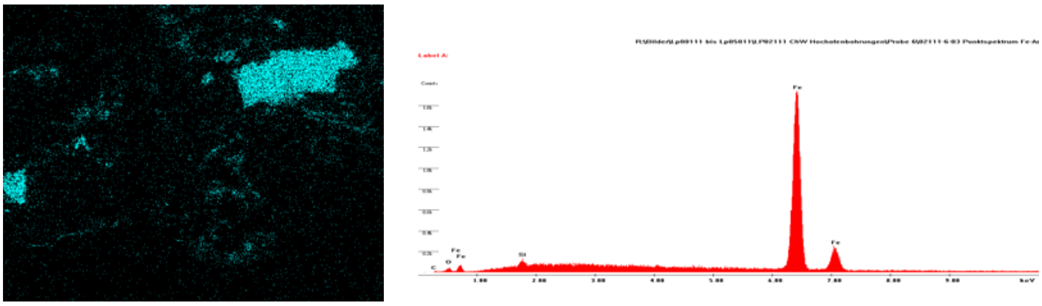


F: SEM contrast of composition *G: C-Distribution* *H: Ti-Distribution*



I: Ti-Distribution *J: EDX-pointgraph of the Ti-enrichment from picture*

Figure 11. Investigation of the sample Section 6 bottom nº 5.

In higher magnification a titanium enclosure inside the carbon phase is detectable (F). A point EDX spectrum detects only the element Titanium without the presence of other elements. It is important to know that the presence of nitrogen is difficult to detect with the used EDX, the lower detection limit is approximately 10%.

The area of the left arrow with the Ti enrichment was investigated in higher magnification. The image F to I shows the titanium grain in detail with the Ti-, C-distribution. The EDX graph evidences only the presence of Titanium.

These examinations indicate that by the infiltration of liquid hot metal and slag high refractory TiCN/TiN compounds are formed and deposited on the microscopic porosity surfaces.

The chemical analysis of core boring samples is given in Table 5.

Table 5. Chemical analysis of core boring sample

	Fe	Si	Al	Ca	Mg	Ti	S
	%	%	%	%	%	%	%
section 4 from hearth level 5	46	5,6	2,7	7,8	1,5	0,5	0,7
section 6 bottom layer 5	4,7	16	5,7	25	16	0,7	1,1

Evidence that continues coinjection of PCI and Rutilit NF contributed to the formation of protective skulls at the critical locations in hearth and bottom. The chemical analysis shows significant changes of Fe, Si, Ca and Mg content from hearth to the bottom. But the Titanium content in both sample are approx. at the same level. These findings deliver the necessary evidence that continues coinjection of PCI and Rutilit NF contributed to the formation of protective skulls at the critical locations in hearth and bottom.

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5 CONCLUSION

At Rogesa Nº 5 Blast Furnace was relined from July to October 2010 after a campaign of 13 years and a cumulative production of 29,1 M t of hot metal. During the campaign an interim repair had to be carried out in 2005 because of progressive wear of the hearth walls.

The use of titanium products was initiated before the interim repair and after the reset the coinjection of pulverized coal and Rutilit NF was developed. The temperature patterns of the hearth walls show the effectiveness of this procedure.

After stopping the hearth walls were dissected and the different carbon block qualities showed specific results of the wear behaviour like the formation of a brittle layer. After the stop also core borings were carried out in order to check the wear of the carbon. Titanium residuals were analysed which formed a protective layer during the coinjection periods.

Furthermore, the injection campaign at Rogesa blast furnaces showed that the coinjection of Rutilit NF and coal will to be a suitable measure for the long term protection of hearth and bottom of blast furnace.

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